The influence of annealing temperature on the morphology of graphene islands*

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(Received 21 March 2012; revised manuscript received 17 April 2012)

We report on temperature-programmed growth of graphene islands on Ru (0001) at annealing temperatures of 700 °C, 800 °C, and 900 °C. The sizes of the islands each show a nonlinear increase with the annealing temperature. In 700 °C and 800 °C annealings, the islands have nearly the same sizes and their ascending edges are embedded in the upper steps of the ruthenium substrate, which is in accordance with the etching growth mode. In 900 °C annealing, the islands are much larger and of lower quality, which represents the early stage of Smoluchowski ripening. A longer time annealing at 900 °C brings the islands to final equilibrium with an ordered moiré pattern. Our work provides new details about graphene early growth stages that could facilitate the better control of such a growth to obtain graphene with ideal size and high quality.

Keywords: graphene islands, Ru (0001), annealing temperature, scanning tunneling microscope

PACS: 81.05.ue, 87.64.Dz, 81.10.Pq **DOI:** 10.1088/1674-1056/21/8/088102

Graphene, a two-dimensional material consisting of sp^2 carbons, has attracted much attention since its initial discovery.[1,2] The growth methods of graphene have developed rapidly to meet the needs of fundamental studies and future applications. Among them, epitaxial growth of graphene on metals[3−10] is extremely important as it holds the potential to produce large-area and high-quality graphene. Moreover, epitaxial graphene has many interesting properties due to the interaction with the substrate,[11−16] and this interaction can be tuned by intercalations of different materials,[17] especially silicon,[18,19] to realize multiple applications. In order to control the growth of graphene, many studies have focused on the growth mechanism[20−23] and the roles of growth parameters, including different kinds of carbon sources,[24,25] annealing temperatures, and annealing times,[26,27] growth pressures,[28] and so on.

Graphene islands (GIs) not only present an opportunity to study the graphene early growth phase but also have many interesting properties due to size confinement and edge effect.[25,29,30] Temperature-programmed growth (TPG), which consists of room temperature (RT) carbon source adsorption and annealing at a certain high temperature, is the most commonly used way of growing epitaxial GIs on metals. Previous work has shown that temperature has a very strong influence on GI sizes and shapes.[26] Moreover, a different annealing temperature in growth may also yield GIs with a different intensity of interaction with the substrate.[27] The present work focuses on the influence of annealing temperature on the sizes and quality of GIs on Ru (0001), which may facilitate the future work that requires GIs with certain sizes.

Our experiments are done in an ultrahigh vacuum (UHV) system with a base pressure of better than 1×10^{-8} Pa. The system is equipped with a commercial scanning tunneling microscope (STM), an electron beam heater (EBH) and a gas station that can introduce ethylene or oxygen into the chamber through a leak valve. The ethylene and oxygen gases are both 99.995% pure. Single-crystal Ru (0001), purchased from MaTeck, is used as a substrate for the epitaxial growth of GIs. The Ru (0001) is treated by Ar^+ sput-

*Project supported by the National Basic Research Program of China (Grant Nos. 2011CB932700, 2010CB923004, 2010CB923004, and 2009CB929103), the National Natural Science Foundation of China (Grant Nos. 10834011 and 60976089), and the Main Direction Program of Knowledge Innovation of the Chinese Academy of Sciences (Grant No. KJCX2-YW-W22).

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tering and annealing in oxygen at a high temperature to yield a clean surface. The method of growing GIs is TPG. In this case ethylene is used to deposit 100 L on the Ru (0001) substrate at room temperature, followed by annealing at a certain high temperature. The sample is kept at that temperature for 30 s and then cooled to room temperature at a rate of 0.5 °C·s^{-1}. To avoid carbon segregation into the Ru bulk,[31] the highest annealing temperature we use is 900 °C. All the samples are scanned by STM in a constant current mode.

In TPG, the carbon amount for graphene growth is fixed. All ethylene molecules adsorbed at the Ru (0001) surface are dehydrogenized at about 500 °C and produce about 0.25-ML carbon on the substrate surface.[23] From then on, no carbon is introduced into the system. So no matter what the annealing temperature is, as long as it is below the carbon segregation temperature, there will always be GIs on the surface. The temperature can affect only the size and density of the GIs.

Figure 1 shows three samples obtained at different annealing temperatures, i.e., 700 °C (Fig. 1(a)), 800 °C (Fig. 1(b)), and 900 °C (Fig. 1(c)). The size distributions of the islands by different temperatures are shown in Fig. 1(d). For 700-°C annealing, the islands are quite small. Entire islands can easily be captured in a 200 nm×200 nm image. The islands that grow by 800-°C annealing are only slightly bigger than those grown at 700 °C. In Fig. 1(b), the bright round protrusions of about 10 nm are argon gas bubbles trapped in the Ru substrate during sputtering. However, when the sample is annealed to 900 °C, the size of the islands increases dramatically. In some areas we scanned, no island edges could be captured, while in some other areas no graphene exists, which means the GIs must be over 1 μm in lateral size and have a very low density.

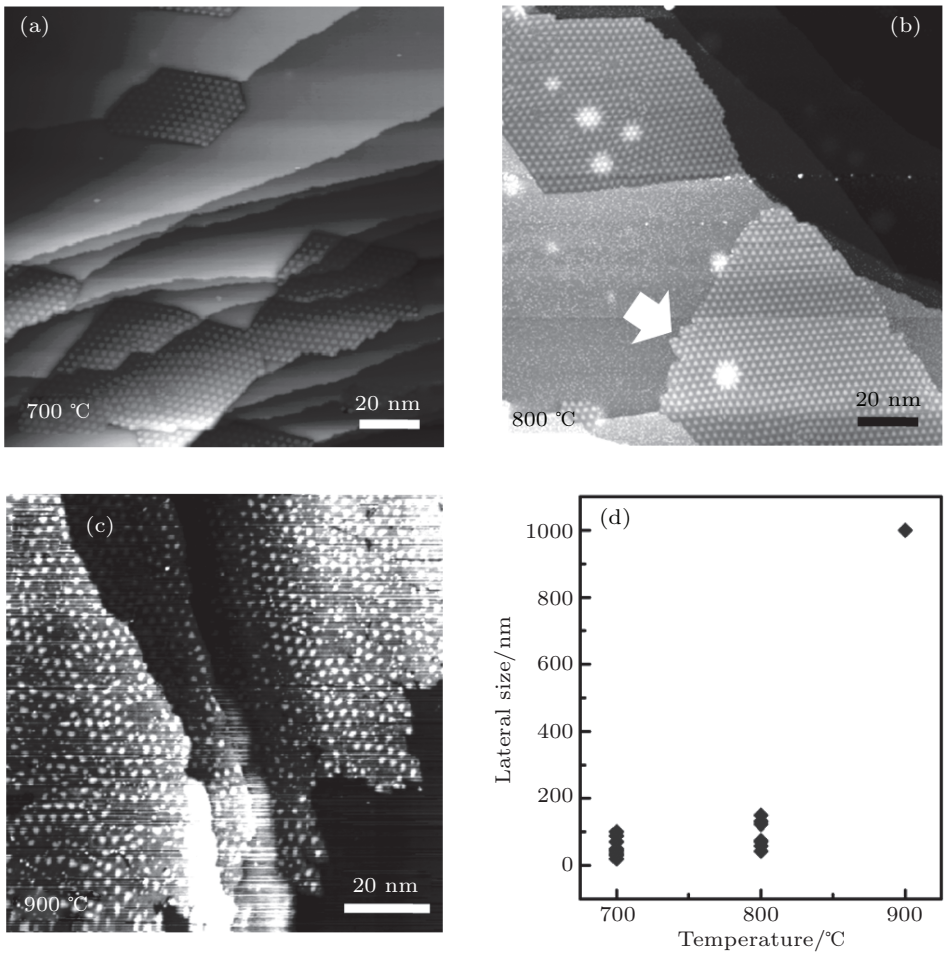


Fig. 1. STM images of TPG GIs on Ru (0001) surface at annealing temperatures of 700 °C (a), 800 °C, (b) and 900 °C (c). (d) The distribution of island sizes yielded at different annealing temperatures.

Besides sizes, the qualities of the GIs are also different. The GIs on the sample annealed to 700 °C as shown in Fig. 1(a), have compact shapes and well defined edges, which are close to equilibrium. If the sample is annealed to 800 °C, the GIs also have a compact structure within the island, which can be verified by a highly ordered moiré pattern; but some edges as indicated by the solid arrow in Fig. 1(b), are coarse. Furthermore, if the annealing temperature is 900 °C, the island itself becomes disordered and the edges are even rougher, which seems to be a patchwork of many small segments.

Figure 2 shows the GIs grown by 800-°C annealing. These GIs have two kinds of edges: the straight ones and the coarse ones as indicated by the empty and solid arrows in Fig. 2(a). After carefully analysing many GIs grown at 800 °C, we find that the straight edges are always the ones that grow along the uphill direction of the substrate steps, while the coarse ones grow downhill. According to the relationship of their growth front and the substrate steps, these edges are named ascending edges and descending edges, respectively. Some previous studies have revealed that graphene nucleates at the lower step edge of the substrate, and then it mainly grows downhill.[6] The uphill growth can also occur by the etching away of some substrate atoms along the step.[21,22] Consequently, in Fig. 2(a), the ascending edge seems to be embedded into the upper step of Ru (0001), which means that this kind of edge is bonded to the Ru edge and relatively inert. On the contrary, the descending edge is free and highly active, which gives rise to easy attachment of new C species. Some researchers[32−34] suggested that the carbon attachment for graphene on metals is based on a precursor of a 5- or 6-atom carbon cluster. After attachment to the edge, the clusters will reshape into a graphene lattice, and then finally relax to a straight edge to meet the energy minimum. From the atomic resolution images in Figs. 2(b) and 2(c) it follows that the ascending edge and also almost all of the descending edge are aligned along the zigzag direction of graphene. These well crystallized edges indicate that GIs are quite close to equilibrium in 800-°C TPG. However, at 800 °C, the mobility of the carbon cluster is still quite high. There are always small carbon clusters diffusing to the edge and coalescing into large islands, which leaves no time for relaxation of the large island edges and gives rise to the coarse shape of the descending edges that have lower attachment energy barriers.

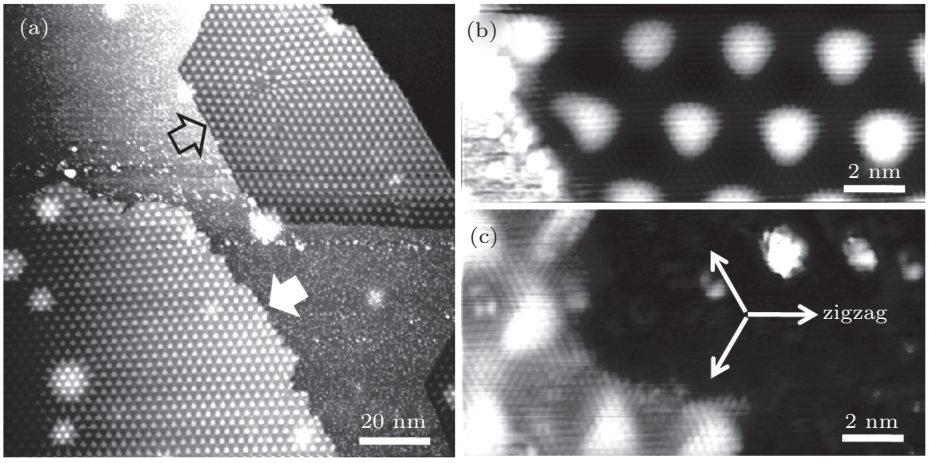


Fig. 2. STM images on GIs grown by 800-°C annealing. (a) The straight ascending edge (indicated by the empty arrow) and the coarse descending edge (indicated by the solid arrow). Panels (b) and (c) are atomic resolution images of the ascending and descending edges, respectively. The three arrows in panel (c) show the zigzag direction of graphene in panels (b) and (c).

The GIs grown by 900-°C annealing are quite different from the ones discussed above as already indicated in Fig. 1. More details within the island and at the edge are shown in Figs. 3(a) and 3(b). In both images, the moiré pattern, which is due to ordered interaction between lattices of graphene and Ru (0001), is fragmentary. Moreover, there are some holes in the GI as indicated by the circles in Fig. 3(b). All these features show that the GI seems to be a patchwork of many small islands. This is in accordance with Smolu-

chowski ripening,[23,26,35] i.e. a small island moves as a whole to coalesce into a larger island. At 900 °C, which is relatively high for graphene growth on Ru (0001), the precursors quickly diffuse and coalesce into small islands. However, at this temperature, these small islands are also highly movable and can diffuse a long distance on the surface. This is different from the GIs grown at lower temperatures, whose precursors are small C_5 or C_6 clusters and the islands are unable to diffuse when they are still quite small (< 200 nm in lateral size). The islands at 900 °C, however, only stop diffusing when they coalesce into extremely large islands, which are, in our case, more than 1-μm across.

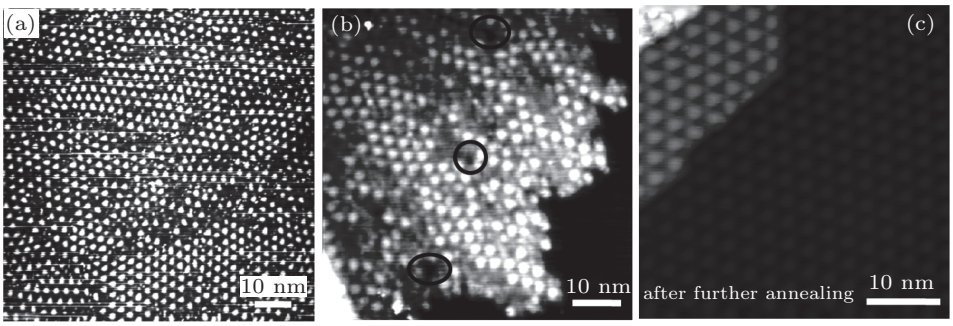


Fig. 3. STM images on GIs grown by 900-°C annealing. Panels (a) and (b) show the moiré patterns within the island and at the edge of the island, respectively. (c) The same sample after further annealing for 10 min.

After the big GIs settle down on the surface, they need time to relax to equilibrium and repair the defects along the boundaries of their component islands. However, at the early stage of the formation of the large islands, so many small islands coalesce and bring along defects that increase dramatically in a very short time. The energy needed for repairing these defects is relatively high. Quick annealing (30 s) and cooling (0.5 °C·s^{-1}) do not provide enough energy for the repair process, so the large islands "freeze" at an early stage where the defects along the component island boundaries still exist. Accordingly, the edge of a coalesced island has many protrusions and is composed of many segments that were previously small islands. If we further anneal this sample for another 10 min, the defects within the islands will be repaired, and an almost perfect graphene moiré pattern will be obtained as shown in Fig. 3(c).

The increase of annealing temperature brings more energy for larger precursors to diffuse on the surface. At 700 °C or 800 °C, the precursors are very small carbon clusters containing only several atoms. These clusters diffuse and coalesce into nearby islands that settle at the step edge of the substrate. However, at 900 °C, these small clusters quickly form small islands, and the resulting small islands of tens of nanometers can also diffuse as precursors until they eventually form immobile large islands. The resulting large islands have many defects that are brought about by incomplete coalescing of the small islands, and they need time to relax into a perfect lattice. So at 900 °C, there is competition between coalescence and relaxation. For the first annealing for 30 s, coalescence is the main growth activity and there is not enough time for the islands to repair the defects; during further annealing for 10 min, as there are already immobile large islands on the surface, coalescence rarely happens and the islands have enough time to relax to equilibrium.

In conclusion, we grew GIs on Ru (0001) surface using TPG on three samples at different annealing temperatures of 700 °C, 800 °C, and 900 °C. The sample annealed to 700 °C has the smallest and the most compact GIs. The GIs grown at 800 °C are only slightly larger than those grown at 700 °C and have a coarse descending edge, which is due to the incessant attachment of small carbon clusters. At an annealing temperature of 900 °C, the GIs grow dramatically larger but with lower quality, which may be due to Smoluchowski ripening of small island diffusion and a competition between coalescing of the component islands and relaxation of the large island as a whole to equilibrium. The quality can be recovered by further annealing of the sample, which confirms that coalescing happens very quickly at the early stage of annealing, while relaxation needs much more time. Our work provides new details about the influence of annealing temperature on GIs/Ru (0001) and could be conducive to better controlling the growth of GIs to

obtain ideal sizes and quality.

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